

The model of a hypothetical room-temperature superconductor.

Konstantin V. Grigorishin* and Bohdan I. Lev†

Boholyubov Institute for Theoretical Physics of the National Academy of Sciences of Ukraine, 14-b Metrolohichna str. Kiev-03680, Ukraine.

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The model of hypothetical superconductivity, where the energy gap asymptotically approaches zero as temperature increases, has been proposed. Formally the critical temperature of such a superconductor is equal to infinity. For practical realization of the hypothesis a superconducting material with such properties is predicted.

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I. INTRODUCTION

A main problem of technical application of superconductors consists in that their critical temperatures T_C are considerably lower than room temperature. The critical temperature depends on an effective coupling with some collective excitations $g = \nu_F \lambda$ (here ν_F is a density of states at Fermi level, λ is an interaction constant) and on energy of the collective excitations ω . Most often a phonon mechanism results in superconductivity, then g is an electron-phonon coupling constant (in most cases $g \lesssim 1$), and ω is a characteristic phonon frequency $\omega \sim 100 \div 400$ K (here $\hbar = k_B = 1$). The larger coupling constant, the larger critical temperature. At large g (as a rule for $g > 10$) we have following expressions for the critical temperature [1, 2]:

$$T_C \propto \omega g \quad - \quad \text{BCS theory} \quad (1)$$

$$T_C \propto \omega \sqrt{g} \quad - \quad \text{Eliashberg theory} \quad (2)$$

Formally the critical temperature can be made arbitrarily large by increasing the electron-phonon coupling constant $T_C(g \rightarrow \infty) \rightarrow \infty$. However, in order to reach room temperature such values of the coupling constant are necessary, which are not possible in real materials. Moreover we can increase the frequency ω due nonphonon pairing mechanisms, as proposed in [2]. However with increasing of the frequency the coupling constant decreases as $g \propto 1/\omega$, therefore

$$T_C(\omega \rightarrow \infty) = 1.14\omega \exp\left(-\frac{1}{g}\right) \rightarrow 0. \quad (3)$$

Many different types of superconducting materials with a wide variety of electron pairing mechanisms exist, however all they have the critical temperature limited by values $\lesssim 100$ K, despite the fact that the highly exotic mechanisms have been proposed. In a present work we propose a fundamentally different approach to the problem of room-temperature superconductivity. This approach is not associated with increasing of the coupling constant or with change of the frequency, but it allows to circumvent the problem in the sense that, having the interaction of conventional intensity (which generates an energy gap $\Delta \sim 10 \div 100$ K), we change ratio between the gap and the critical temperature as $2\Delta/T_C \rightarrow 0$ instead of a finite value $3 \div 7$ for presently known materials.

II. GENERAL IDEA.

First of all we propose a principal possibility to increase the critical temperature due to generalization of BCS model in the following sense: let us consider a system of fermions with Hamiltonian:

$$\hat{H} = \sum_{\mathbf{k}, \sigma} \xi(k) a_{\mathbf{k}, \sigma}^\dagger a_{\mathbf{k}, \sigma} - \frac{\lambda}{V} \sum_{\mathbf{p}, \mathbf{p}'} a_{\mathbf{p} \uparrow}^\dagger a_{-\mathbf{p} \downarrow}^\dagger a_{-\mathbf{k} \downarrow} a_{\mathbf{k} \uparrow} + v \sum_{\mathbf{k}} \left[\frac{\Delta}{|\Delta|} a_{\mathbf{k} \uparrow}^\dagger a_{-\mathbf{k} \downarrow}^\dagger + \frac{\Delta^+}{|\Delta|} a_{-\mathbf{k} \downarrow} a_{\mathbf{k} \uparrow} \right] \equiv \hat{H}_{\text{BCS}} + \hat{H}_{\text{ext}}, \quad (4)$$

*Electronic address: gkonst@ukr.net

†Electronic address: bohdan.lev@gmail.com

where \hat{H}_{BCS} is BCS Hamiltonian - kinetic energy + pairing interaction ($\lambda > 0$), energy $\xi(k) \approx v_F(|\mathbf{k}| - k_F)$ is counted from Fermi surface. The term \hat{H}_{ext} is the external pair potential or "source term" [3]. For example, in ferromagnetism a term \mathbf{SH} - the energy of a spin in an external magnetic field plays a role the source term \hat{H}_{ext} . Operators $a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+$ and $a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}$ are creation and annihilation of Cooper pair operators [4], Δ and Δ^+ are anomalous averages:

$$\Delta^+ = \frac{\lambda}{V} \sum_{\mathbf{p}} \langle a_{\mathbf{p}\uparrow}^+ a_{-\mathbf{p}\downarrow}^+ \rangle, \quad \Delta = \frac{\lambda}{V} \sum_{\mathbf{p}} \langle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \rangle, \quad (5)$$

which are the complex order parameter $\Delta = |\Delta|e^{i\theta}$ (the energy gap Δ is analogous to magnetization $\mathbf{M} = \langle \mathbf{S} \rangle$ in ferromagnetism). The multipliers $\frac{\Delta}{|\Delta|}$ and $\frac{\Delta^+}{|\Delta|}$ are introduced into \hat{H}_{ext} in order that the energy does not depend on the phase θ ($a \rightarrow ae^{i\theta/2}, a^+ \rightarrow a^+ e^{-i\theta/2} \Rightarrow \Delta \rightarrow \Delta e^{i\theta}, \Delta^+ \rightarrow \Delta^+ e^{-i\theta}$). Thus both \hat{H}_{BCS} and \hat{H}_{ext} is invariant under the $U(1)$ transformation unlike the source term in [3] where it has a noninvariant form $v \sum [a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ + a_{-\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}]$. Hence v is energy of a Cooper pair relative to uncoupled state of the electrons in the external pair potential H_{ext} . It should be noted that the energy gap $|\Delta|$ is energy of a Cooper pair relative to uncoupled state of the electrons too. However the field Δ is a self-consistent field as a consequence of attraction between electrons. The field v is the applied field to the system from the outside.

Using the Fermi commutation relations and the anomalous averages (5), the Hamiltonian (4) can be rewritten in a form [5]:

$$\hat{H} = \sum_{\mathbf{k}, \sigma} \xi(k) a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} + \left(1 - \frac{v}{|\Delta|}\right) \sum_{\mathbf{k}} \left[\Delta^+ a_{\mathbf{k}\uparrow} a_{-\mathbf{k}\downarrow} + \Delta a_{-\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow}^+ \right] + \frac{1}{\lambda} V |\Delta|^2. \quad (6)$$

Then normal G and anomalous F propagators have forms:

$$G = i \frac{\varepsilon_n + \xi}{(i\varepsilon_n)^2 - \xi^2 - |\Delta|^2(1 - v/|\Delta|)^2} \quad (7)$$

$$F = i \frac{\Delta(1 - v/|\Delta|)}{(i\varepsilon_n)^2 - \xi^2 - |\Delta|^2(1 - v/|\Delta|)^2}, \quad (8)$$

where $\varepsilon_n = \pi T(2n + 1)$ [6]. Then from Eq.(5) we have self-consistency condition for the order parameter

$$\Delta = \lambda \nu_F T \sum_{n=-\infty}^{\infty} \int_{-\omega}^{\omega} d\xi i F(\varepsilon_n, \xi) \Rightarrow 1 = g \int_{-\omega}^{\omega} d\xi \frac{1 - v/|\Delta|}{2\sqrt{\xi^2 + |\Delta|^2(1 - v/|\Delta|)^2}} \tanh \frac{\sqrt{\xi^2 + |\Delta|^2(1 - v/|\Delta|)^2}}{2T}. \quad (9)$$

Solutions of Eq.(9) are shown in Fig.1. If the external pair potential is absent $v = 0$ we have usual self-consistency equation for the gap Δ : the gap is a function of temperature such that $\Delta(T \geq T_c) = 0$. The larger coupling constant $g = \lambda \nu_F$, the larger T_c . If $v > 0$ then the pairing of quasiparticles results in increase of the system's energy that suppresses superconductivity and first order phase transition takes place. If $v < 0$ then the pairing results in decrease of the system's energy. In this case a solution of Eq.(9) is such that the gap Δ does not vanish at any temperature. At large temperature $T \gg \omega, |v|$ the gap is

$$|\Delta(T \rightarrow \infty)| = \frac{g\omega|v|}{2T}. \quad (10)$$

Hence the critical temperature is $T_c = \infty$ (in reality it limited by the melting of the substance). In ferromagnetism if the external magnetic field \mathbf{H} presents then the magnetization exists at any temperature and $\mathbf{M}(T \rightarrow \infty) \rightarrow 0$. It should be noted that if $\lambda = 0$ then for any v a superconducting state does not exist ($\Delta = 0$ always). This means electron-electron coupling is the cause of the transition to superconducting state only but not the external pair potential v . This fact is a peculiarity of superconductivity and it does not have analogous in ferromagnetism. The theory of superconductivity with Hamiltonian (4) has been developed in a work [10] similarly to Ginzburg-Landau theory, the effect of a Coulomb pseudopotential has been investigated in a work [11].

Let us take into account the fact that electron-phonon interaction $gD(\omega(\mathbf{q}))$ leads to superconductivity, where D is a phonon propagator. Eliashberg equations [1, 2], unlike BCS equations, can describe renormalization of quasiparticles' mass and decrease of effectiveness of the interaction at phonon energies $\omega(\mathbf{q}) \lesssim T$ - difference of the asymptotics (1) and (2). However these facts does not change the previous conclusions. In [7-9] a method to consider electron-phonon

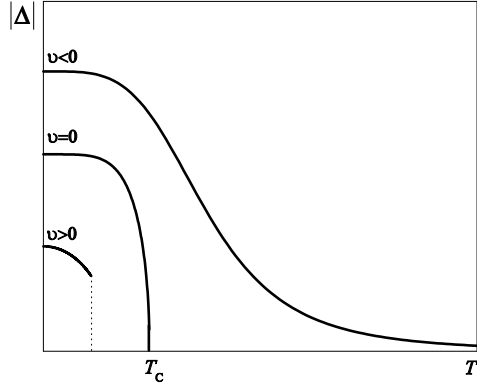


Figure 1: Energy gaps $\Delta(T)$ as solution of Eq.(9) for three values of the external pair potential v .

interaction has been proposed, however the resulting equation is much simpler than Eliashberg equations. Phonons are dispersionless $\omega(q) = \omega$ and the electron-phonon coupling constant does not depend on a wave vector $\lambda(q) = \lambda$ are suggested in this method. The electron-phonon interaction generates the gap via the anomalous propagator F and renormalizes an energetic parameter via the normal propagator G :

$$\begin{aligned}\Delta_n &= \int \frac{d^3p}{(2\pi)^3} \lambda^2 T \sum_{m=-\infty}^{+\infty} iF(\mathbf{p}, \varepsilon_m) iD(\varepsilon_n - \varepsilon_m, \mathbf{k}) \\ &= g \sum_{m=-\infty}^{+\infty} \frac{\pi T \Delta_m}{\sqrt{\tilde{\varepsilon}_m^2 + |\Delta_m|^2}} \frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2}\end{aligned}\quad (11)$$

$$\begin{aligned}\tilde{\varepsilon}_n &= i\varepsilon_n + \int \frac{d^3p}{(2\pi)^3} \lambda^2 T \sum_{m=-\infty}^{+\infty} iG(\mathbf{p}, \tilde{\varepsilon}_m) iD(\varepsilon_n - \varepsilon_m, \mathbf{k}) \\ &= i\varepsilon_n + g \sum_{m=-\infty}^{+\infty} \frac{\pi T i\tilde{\varepsilon}_m}{\sqrt{\tilde{\varepsilon}_m^2 + |\Delta_m|^2}} \frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2},\end{aligned}\quad (12)$$

where $g \equiv \lambda^2 \nu_F \frac{2}{\omega_0}$ is the coupling constant. The phonon propagator can be represented in a form:

$$\frac{\omega^2}{(\varepsilon_n - \varepsilon_m)^2 + \omega^2} \rightarrow \frac{\omega}{\sqrt{\varepsilon_n^2 + \omega^2}} \frac{\omega}{\sqrt{\varepsilon_m^2 + \omega^2}} \equiv w_n w_m, \quad (13)$$

and the gap depends on the energetic parameter as $\Delta_n = \Delta w_n$. Then the energetic parameter is not renormalized: $\tilde{\varepsilon}_n = i\varepsilon_n$, because there is an odd function under the sign of sum in (12) in the approximation (13). Equation for the gap has a form:

$$1 = g \sum_{n=-\infty}^{+\infty} \frac{\pi T w_n^2}{\sqrt{\varepsilon_n^2 + |\Delta|^2} w_n^2} \quad (14)$$

When $T_c \ll \omega$ (small g) Eq.(14) has the asymptotic (3), when $T_c \gg \omega$ (large g) one has the asymptotic (2). Eq.(14) is easier than Eliashberg equations, however one is more correct than BCS equation.

Substituting the propagators (7,8) in Eqs.(11,12) we have an analog of Eq. (9):

$$1 = g \sum_{n=-\infty}^{+\infty} \frac{\pi T (w_n - v/|\Delta|) w_n}{\sqrt{\varepsilon_n^2 + |\Delta|^2} (w_n - v/|\Delta|)^2} \quad (15)$$

If to suppose $v = 0$ then Eq.(15) is transformed into Eq.(14). The function $\Delta(T)$ for the cases $v > 0, v = 0, v < 0$ is the same as in Fig.(1). If $v < 0$ then in a limit $T \gg \omega, |v|$ we have

$$|\Delta(T \rightarrow \infty)| = \frac{2g\omega|v|}{\pi T}. \quad (16)$$

that is analogous to Eq.(10).

III. MODEL OF A SUPERCONDUCTOR.

In the previous section we demonstrated a principal possibility to increase the critical temperature due to the external pairing potential v . In this section we propose a model of the system where such a situation can be realized. Let us consider superconductors alkali-doped fullerenes A_3C_{60} ($A = K, Rb, Cs$). The threefold degenerate t_{1u} level is partly occupied and electrons couple strongly to eight H_g intramolecular Jahn-Teller phonons (electron-vibron interaction). Hamiltonian of the system has a form [12]:

$$\begin{aligned} \hat{H} = & - \sum_{ijm\sigma} t_{ij} a_{im\sigma}^+ a_{jm\sigma} + U \sum_{imm'} n_{im\uparrow} n_{im'\downarrow} + \omega \sum_{i\nu} b_{i\nu}^+ b_{i\nu} \\ & + \lambda \sum_{imm'\sigma\nu} V_{mm'}^{(\nu)} a_{im\sigma}^+ a_{im'\sigma} (b_{i\nu}^+ + b_{i\nu}). \end{aligned} \quad (17)$$

$a_{im\sigma}^+(a_{jm\sigma})$ is the electron creation (annihilation) operator acting on site i , orbital $m = 1, 2, 3$ and spin σ . $b_{i\nu}^+(b_{i\nu})$ is the phonon creation (annihilation) operator with the vibration mode $\nu = 1, \dots, 5$. t_{ij} is the hopping integral, U is the on-site Coulomb interaction, ω is the phonon frequency, and λ is the electron-phonon coupling constant. The coupling matrices $V^{(\nu)}$ are determined by icosahedral symmetry. The dimensionless electron-phonon coupling constant is $g = \frac{5}{3}\lambda^2\nu_F/\omega$. Typical parameters are $g \sim 0.5 \div 1$, $\omega/W \sim 0.1 \div 0.25$ and $U/W \sim 1.5 \div 2.5$, where $W \sim 0.5\text{eV}$ is a electron bandwidth. Basic mechanisms resulting in superconductivity are:

1. The dynamical Jahn-Teller effect (interaction with H_g intramolecular oscillations) favors the formation of a local singlet [13–15]:

$$|\Phi_{0\uparrow\downarrow}\rangle = \frac{1}{\sqrt{3}} \sum_m C_{m\uparrow}^+ C_{m\downarrow}^+ |0\rangle, \quad (18)$$

where the spin-up and spin-down electrons have the same m quantum number, i.e., a local pairing takes place. Here $|0\rangle$ is the neutral C_{60} molecule for the alkali-metal-doped materials, the quantum number m labels the three orthogonal states of t_{1u} symmetry (LUMO state). The normal state (high spin state) of two electrons is

$$|\Phi_{0\uparrow\uparrow}\rangle = C_{m_1\uparrow}^+ C_{m_2\uparrow}^+ |0\rangle. \quad (19)$$

The low-spin state is lower in energy than the high-spin state if $E_{JT} > \frac{2}{3}K$, where $E_{JT} = \frac{\lambda^2}{\omega}$ is a Jahn-Teller energy, K is an exchange integral. For A_xC_{60} ($x = 2, 3, 4$) the coupling with H_g phonons overpowers Hund's rule coupling. Experimental confirmation of this fact is that A_4C_{60} must be anti-ferromagnetic insulator (Hubbard-like model predicts), while it is known experimentally there are no moments in A_4C_{60} .

2. In a work [12] the following result has been obtained. For noninteracting electrons the hopping tends to distribute the electrons randomly over the molecular levels. This makes more difficult to add or remove an electron pair with the same m quantum numbers. However as U is large $U > W$ the electron hopping is suppressed and the local pair formation becomes more important. The Coulomb interaction actually helps local pairing. For A_g phonons, the phonon-induced attractive interaction U_{ph} is of the order of $U_{ph}/W \sim -0.47$. T_C is vanished when $U + U_{ph} \geq 0$. For the Jahn-Teller H_g phonons the attractive interaction is smaller $U_{ph}/W \sim -0.2$. This attractive interaction is, therefore, quickly overwhelmed by the Coulomb repulsion. Superconductivity remains, however, even for $U + U_{ph} \gg 0$, and T_C drops surprisingly slowly as U is increased. The reason is that local pairing arises from correlation of spin and orbital structures within each site, and therefore it is not suppressed by the charge interaction. Superconductivity is expected to exist in this material right up to the Mott transition.

This situation is very different from Eliashberg theory. We can see, because of the local pairing, the Coulomb interaction enters very differently for Jahn-Teller and non-Jahn-Teller models, and it cannot be easily described by a Coulomb pseudopotential: $g - \mu^*$.

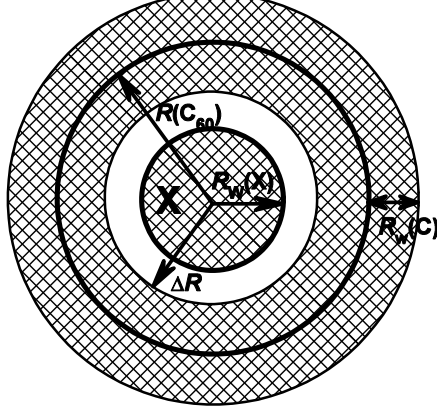


Figure 2: Cross-section of an endohedral fullerene $X@C_{60}$. The carbon cage can be considered as a spherical layer of thickness $2R_W(C)$ and central radius $R(C_{60})$. The central atom X placed into the inner cavity radius of ΔR is a noble gas atom van der Waals radius of $R_W(X)$.

Thus in an alkali-doped fullerene the Cooper pairs are formed on one molecule size of $R = 3.55\text{\AA}$ as result a of electron-vibron interaction and suppression of hopping between molecules with one-site Coulomb interaction U . This situation is fundamentally different from superconductivity in metals, where the size of a Cooper pair is macroscopic quantity $\sim 10^3 \div 10^4\text{\AA}$. Let us consider some features of the molecular structure C_{60} . The van der Waals radius of a carbon atom is $R_W(C) = 1.70\text{\AA}$. Thus a fullerene has an inner cavity in its center the size of $\Delta R = R(C_{60}) - R_W(C) = 1.85\text{\AA}$. A noble gas atom X can be trapped in a carbon cage in the inner cavity (Fig.2) - we have endohedral complexes $X@C_{60}$ [16–22]. Since for a helium atom $R_W(He) = 1.40\text{\AA} < \Delta R$ the atom interacts with the carbon cage by van der Waals interaction only and its electronic shell does not make hybridized orbitals with electronic shells of the carbon cage. If a helium atom is placed into each fullerene molecule in alkali-doped fullerenes then we have hypothetical material $A_3He@C_{60}$. Electronic properties of $A_3He@C_{60}$ must be exactly the same as electronic properties of A_3C_{60} . Changes in oscillation spectrum of a fullerene can be neglected.

As noted above, in an endohedral fullerene the noble gas atom interacts with a carbon cage by van der Waals force. As is well known van der Waals interaction depends on electronic configuration of interacting subsystems. In alkali-doped fullerenes alkali metal atoms give valent electrons to fullerene molecules. Then energy of the van der Waals interaction has to depend on a state of the excess electrons on the surface of a molecule C_{60} . Any two electrons can be in the paired state (18) or in the normal state (19). Let this energy for the paired state is $v_{\uparrow\downarrow}$ and the energy for the normal state is $v_{\uparrow\uparrow}$. If $v_{\uparrow\downarrow} < v_{\uparrow\uparrow}$ then the paired state is more energetically favorable than the normal state: a molecule $X@C_{60}^{n-}$ has lower energy if the excess electrons are in the paired state than the energy if the electrons are in the normal state (if we turn off the electron-electron interaction). On the other hand as noted above for noninteracting electrons the hopping t_{ij} tends to distribute the electrons randomly over the molecular levels thus destroying the local pairs. However the relationship $v_{\uparrow\downarrow} < v_{\uparrow\uparrow}$ makes more energetically favorable to place electrons in a state (18) with the same quantum numbers m and thus it confronts the destruction of local pairs by the hopping. Hence a function

$$v = v_{\uparrow\downarrow} - v_{\uparrow\uparrow} \quad (20)$$

plays the role of the external pair potential. The van der Waals interaction is interaction due to virtual transitions of the Cooper pair from a triply degenerated level t_{1u} ($l = 5$) to levels t_{1g} ($l = 5$), h_g, t_{2u}, h_u ($l = 6$), g_g, g_u, t_g ($l = 7$) [23, 24], where l is an orbital index for π -electrons (we can use a state $C_{m\uparrow}^+ C_{m\downarrow}^+ |0\rangle$ instead of the state (18) for simplicity, because the result will not depend on the quantum number m):

$$\Phi_{0\uparrow\downarrow} \equiv \Omega_{l=5,\gamma}(\mathbf{R}_1)\Omega_{l=5,\gamma}(\mathbf{R}_2) \longleftrightarrow \frac{1}{\sqrt{2}} [\Omega_{l,\gamma'}(\mathbf{R}_1)\Omega_{l=5,\gamma}(\mathbf{R}_2) + \Omega_{l=5,\gamma}(\mathbf{R}_1)\Omega_{l,\gamma'}(\mathbf{R}_2)] \equiv \Phi_{k\uparrow\downarrow}, \quad (21)$$

and of the helium atom from a level $1s$ to levels $2s, 2p, 3s, 3p, 3d \dots$:

$$\begin{aligned} \Psi_0 &\equiv f_{0,0}(r_1)Y_{0,0}(\mathbf{r}_1)f_{0,0}(r_2)Y_{0,0}(\mathbf{r}_2) \\ &\longleftrightarrow \frac{1}{\sqrt{2}} \left[f_{n,l}(r_1)Y_{l,\tilde{m}}(\mathbf{r}_1)f_{0,0}(r_2)Y_{0,0}(\mathbf{r}_2) + f_{0,0}(r_1)Y_{0,0}(\mathbf{r}_1)f_{n,l}(r_2)Y_{l,\tilde{m}}(\mathbf{r}_2) \right] \equiv \Psi_p, \end{aligned} \quad (22)$$

where the index γ labels irreducible representation of icosahedral symmetry group; n, l, m are principal quantum number, orbital quantum number and magnetic quantum number accordingly; $f_{n,l}(r)$ is a radial wave function, $Y_{l,m}$ is a spherical wave functions. Φ_0 and Ψ_0 are ground-states of a Cooper pair and a helium atom accordingly. Φ_k and Ψ_p are the excited states of the Cooper pair and the helium atom accordingly, k and p are sets of quantum indices of the corresponding excited states. \mathbf{R}_1 and \mathbf{R}_2 are radius-vectors of electrons of the Cooper pair, and $|\mathbf{R}_1| \approx |\mathbf{R}_2| \approx R$ since the Cooper pair is on surface of the molecule. \mathbf{r}_1 and \mathbf{r}_2 are radius-vectors of electrons of the helium atom, and $\langle r \rangle = 0.31\text{\AA} \ll R = 3.55\text{\AA}$ - the atom is much less than the fullerene molecule. Signs "+" in the sums are caused by the fact that the ground states of both the Cooper pair and the helium atom are singlet, and transitions between singlet and triplet states are allowed only when there is the spin-orbit interaction, but this interaction can be neglected. Energy of the van der Waals interaction is defined with the second order correction:

$$v_{\uparrow\downarrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle|^2}{E_0 + \tilde{E}_0 - E_k - \tilde{E}_p}, \quad (23)$$

where the summation is made over the indexes of all possible excited states of the Cooper pair k and of the helium atom p ; E_0 and \tilde{E}_0 are ground state energies of the Cooper pair and the helium atom accordingly, E_k and \tilde{E}_p are energies of the corresponding excited states. Since $E_0 < E_k, \tilde{E}_0 < \tilde{E}_p$ then $v_{\uparrow\downarrow} < 0$. An operator of the interaction is (within a single molecule the effects of screening can be neglected)

$$\hat{V}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{R}_2 - \mathbf{r}_2|} - \frac{2e^2}{|\mathbf{R}_1|} - \frac{2e^2}{|\mathbf{R}_2|}. \quad (24)$$

The van der Waals interaction is a high-frequency process because the interaction is result of virtual transitions between atomic (molecular) levels. This means that screening of the interaction must be determined by a high-frequency dielectric function ε_∞ , that is by a plasmon mechanism. However transition between molecular levels of C_{60} , hence between energy bands of K_3C_{60} , takes place. This means that plasmons can not exist with such energies. The frequency of the transitions between the levels of a helium atom is even larger: $\sim 20\text{eV}$. Hence screening of the van der Waals interaction by condition electrons is very inefficient and it can be neglected.

To calculate the energy of van der Waals interaction if electrons are in the normal state (19) we can use an antisymmetric wave function:

$$\begin{aligned} \Phi_{0\uparrow\uparrow} &\equiv \frac{1}{\sqrt{2}} [\Omega_{l=5,\gamma_1}(\mathbf{R}_1)\Omega_{l=5,\gamma_2}(\mathbf{R}_2) - \Omega_{l=5,\gamma_1}(\mathbf{R}_2)\Omega_{l=5,\gamma_2}(\mathbf{R}_1)] \\ &\longleftrightarrow \frac{1}{\sqrt{2}} [\Omega_{l,\gamma'}(\mathbf{R}_1)\Omega_{l=5,\gamma_2}(\mathbf{R}_2) - \Omega_{l,\gamma'}(\mathbf{R}_2)\Omega_{l=5,\gamma_2}(\mathbf{R}_1)] \equiv \Phi_{k\uparrow\uparrow}. \end{aligned} \quad (25)$$

Energy of the van der Waals interaction is

$$v_{\uparrow\uparrow} = \sum_{k,p} \frac{|\langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle|^2}{E_0 + \tilde{E}_0 - E_k - \tilde{E}_p}. \quad (26)$$

It should be noted that due to electroneutrality of a helium atom and small size of the atom compared to radius of the molecule $\langle r \rangle = 0.31\text{\AA} \ll R = 3.55\text{\AA}$ we have that $\langle 00|V|00 \rangle = 0$ - the first order process can be neglected. Moreover we can neglect the exchange processes between the helium atom and electrons on the molecule's surface, that can not be done, for example, for atoms Ar and Xe due to a not small overlap of the atom's wave functions with the wave functions of electrons on the fullerene cage [25–28]. In this work we neglect the higher order processes, i.e. non-additivity of van der Waals interaction between the helium atom, the pair of excess electrons and the carbon cage of a fullerene molecule.

To estimate v a fullerene molecule can be considered as a sphere, that simplifies the calculation of the matrix elements $\langle kp|V|00 \rangle$. Then the wave functions on the fullerene's surface $\Omega_{l,\gamma}$ are spherical wave functions $Y_{l,m}$, where l and m is orbital quantum number and magnetic quantum number accordingly, $|\mathbf{R}_1| = |\mathbf{R}_2| = R$. Energy of each level is

$$E_l = \frac{\hbar^2 l(l+1)}{2m_e R^2}. \quad (27)$$

In a ground state $l = 5$ each state is degenerated in $m = -l \dots l$. The wave function of a Cooper pair in the ground state is

$$Y_{5,m}(\mathbf{R}_1)Y_{5,m}(\mathbf{R}_2), \quad (28)$$

and the wave function of some a excited state is:

$$\frac{1}{\sqrt{2}} [Y_{l',m'}(\mathbf{R}_1)Y_{5,m}(\mathbf{R}_2) + Y_{5,m}(\mathbf{R}_1)Y_{l',m'}(\mathbf{R}_2)], \quad (29)$$

where $l' > 5$, $m' = -l' \dots l'$. The antisymmetric wave functions are

$$\frac{1}{\sqrt{2}} [Y_{5,m_1}(\mathbf{R}_1)Y_{5,m_2}(\mathbf{R}_2) - Y_{5,m_1}(\mathbf{R}_2)Y_{5,m_2}(\mathbf{R}_1)] \longleftrightarrow \frac{1}{\sqrt{2}} [Y_{l',m'}(\mathbf{R}_1)Y_{5,m_2}(\mathbf{R}_2) - Y_{l',m'}(\mathbf{R}_2)Y_{5,m_2}(\mathbf{R}_1)]. \quad (30)$$

It should be noted that in this case the energies of van der Waals interaction (23) and (26) are functions of the magnetic quantum number: $v_{\uparrow\downarrow}(m)$, $v_{\uparrow\uparrow}(m)$. Below we will calculate v for each m . The Coulomb potential is convenient to be expanded in spherical harmonics:

$$\frac{1}{|\mathbf{R} - \mathbf{r}|} = \begin{cases} \frac{4\pi}{R} \sum_{L,M} \frac{1}{2L+1} \left(\frac{r}{R}\right)^L Y_{L,M}^+(\theta, \varphi) Y_{L,M}(\Theta, \Phi), & r < R \\ \frac{4\pi}{r} \sum_{L,M} \frac{1}{2L+1} \left(\frac{R}{r}\right)^L Y_{L,M}^+(\theta, \varphi) Y_{L,M}(\Theta, \Phi), & r > R \end{cases}, \quad (31)$$

where $M = -L, -L+1 \dots L$. Since $\langle r \rangle = 0.31\text{\AA} \ll R = 3.55\text{\AA}$ then the expansion at $r > R$ can be omitted. The matrix element of the interaction can be represented as

$$\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle = 2e^2 \sum_{L,M} ABC, \quad (32)$$

where

$$\begin{aligned} A &= \frac{4\pi}{R} \frac{1}{2L+1} \int_0^\infty f_{n,\tilde{l}}^+ f_{0,0} r^2 \left(\frac{r}{R}\right)^L dr \\ B &= \int Y_{\tilde{l},\tilde{m}}^+ Y_{0,0} Y_{L,M}^+ \sin \theta d\theta d\varphi \\ C &= \int Y_{l',m'}^+ Y_{5,m} Y_{L,M} \sin \Theta d\Theta d\Phi \end{aligned}$$

Transitions to states $l' = 6$ for a Cooper pair and to states $2p, 3p, 4d$ for a helium atom when the magnetic quantum numbers change as $m' - m = \tilde{m} = 0, \pm 1$ give the largest contribution to Eq.(32). $E_{5,m} - E_{6,m'} \approx 3.6\text{eV}$, $\tilde{E}_{0,0,0} - \tilde{E}_{n,\tilde{l},\tilde{m}} \approx 21\text{eV}$. Calculation shows that v is almost independent of m :

$$v_{\uparrow\downarrow}(m = 0 \dots \pm 5) \approx -80\text{K}, \quad (33)$$

that indicates the correctness and usability of the spherical wave functions instead of the functions (21) to estimate the potential v . Moreover the matrix element $\langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle$ does not depend on m_2 . It is easy to show that each matrix element $\langle \Phi_{[l,m,l',m']\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{[l,m]\uparrow\downarrow} \rangle$ corresponds to the element $\langle \Phi_{[l,m_2,l',m']\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{[l,m_1,m_2]\uparrow\uparrow} \rangle$ where $l' = l'$, $m' - m = m' - m_1$. Then we can find that

$$\langle \Phi_{k\uparrow\downarrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\downarrow} \rangle = \sqrt{2} \langle \Phi_{k\uparrow\uparrow}, \Psi_p | \hat{V} | \Psi_0, \Phi_{0\uparrow\uparrow} \rangle \quad (34)$$

for the corresponding matrix elements. Hence we have

$$v_{\uparrow\downarrow} = 2v_{\uparrow\uparrow} \quad (35)$$

Thus a fullerene molecule with excess electrons has a lower energy if the electrons are in the paired state (18) than energy if the electrons are in the state according to Hund's rule (19). For each pair the energy gain is $v = -40\text{K}$ - Eq.(20). The reason of the relation (34) consists in the fact that if electrons are in different states (with $m_1 \neq m_2$ - Eq.(30)) then the probability amplitude is parted into two mutually orthogonal parts with the weights $1/\sqrt{2}$ each. It should be noted that for symmetric combination with $m_1 \neq m_2$ - a plus sign instead of a minus sign in Eq.(30) the result is the same.

To estimate the energy gap Δ we can use the continuum approximation (15) instead the Habbard hamiltonian (18). The characteristic frequency of intramolecular H_g oscillations can be taken as the effective frequency ω . Let the frequency is $\omega/W = 0.1$ where $W = 0.5\text{eV}$ is the electron bandwidth. The effective coupling constant g must be such that the critical temperature calculated with Eq.(14) is equal to critical temperature $T_c = 19.3\text{K}$ of K_3C_{60} , then we have $g = 0.283$. The functions $\Delta(T)$ calculated with Eqs.(14,15) are shown in Fig.3. We can see for $v < 0$ the gap tends to zero asymptotically with increasing temperature. Thus the critical temperature is equal to infinity, in practice it is limited by the melting point of the substance.

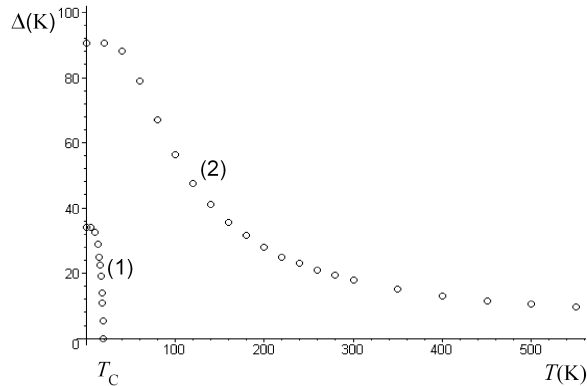


Figure 3: Energy gaps $\Delta(T)$ as solution of Eq.(14) for K_3C_{60} with critical temperature $T_C = 19.3K$ - a curve {1}, as solution of Eq.(15) for $K_3He@C_{60}$ with the external pair potential $v = -40K$ - a curve {2}.

IV. CONCLUSION.

In this work a model of a hypothetical room-temperature superconductor has been proposed. Our idea is based on the fact that the phase independent external pair potential can be added in BCS Hamiltonian - Eq.(4). This field acts on a Cooper pair changing its energy relative to uncoupled state of the electrons. In a case of increasing of Cooper pair's energy by the external pair field a suppression of superconductivity takes place. In a case of decreasing of Cooper pair's energy by the field the energy gap tends to zero asymptotically with increasing temperature - Fig.1. Thus the ratio between the gap and the critical temperature is $2\Delta/T_C = 0$ instead of a finite value in BCS theory. For practical realization of this model we propose a hypothetical superconductor on the basis of alkali-doped fullerenes K_3C_{60} or Rb_3C_{60} with the use of endohedral structures $He@C_{60}$, where a helium atom is in the center of each fullerene molecule. According to [12–15] in alkali-doped fullerene Cooper pairs are formed on surface of the fullerene molecules due electron-vibron interaction and suppression of hopping between molecules by one-site Coulomb interaction. In an endohedral fullerene the noble gas atom interacts with a carbon cage by van der Waals force. The van der Waals interaction depends on a state of excess electrons on surface of the molecule. We have shown that energy of the molecule if the excess electrons on its surface are in the paired state (18), when two electrons are in a state with the same quantum numbers, is lower than the energy if the electrons are in the normal state (19), when the electrons are in a state with different quantum numbers and maximal spin. It makes more energetically favorable to place electrons in the state with the same quantum numbers m , that resists the destruction of local pairs by the hopping between molecules. Thus difference of the energies of the van der Waals interaction plays a role of the external pair potential $v < 0$. We have calculated the temperature dependence of the energy gap for a hypothetical material $K_3He@C_{60}$ using the continuum approximation (15) with an effective electron-phonon interaction - Fig.3. In this material the superconducting phase exists at any temperature unlike the pure system K_3C_{60} where the phase is limited by the finite critical temperature.

In connection with the obtained results it should be noted that in works [29, 30] it had been reported about the synthesis of the first endohedral fullerene superconductors $A_3Ar@C_{60}$ having critical temperatures on 2 – 3 kelvins less than critical temperatures of the pure materials A_3C_{60} . The van der Waals radius of Ar is slightly more than radius of the inner cavity in center of a fullerene molecule. In this case an overlap of the argon atom's wave functions with the wave functions of electrons on the fullerene cage takes place, hence the exchange interaction plays a role. The radii of Kr and Xe are much larger hence role of the exchange interaction is more significant. Thus the influence of Ar, Kr, Xe requires special consideration that goes beyond the present work.

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